

REC'D 26 MAR 2001

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference SR 18544 US/PA	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/US99/29666	International filing date (day/month/year) 13/12/1999	Priority date (day/month/year) 30/12/1998
International Patent Classification (IPC) or national classification and IPC B01J20/18		
Applicant THE REGENTS OF THE UNIVERSITY OF MICHIGAN et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.



2. This REPORT consists of a total of 6 sheets, including this cover sheet.

- ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 4 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☒ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand 15/07/2000	Date of completion of this report 22.03.2001
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Jourdan, A Telephone No. +49 89 2399 8349 

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/US99/29666

I. Basis of the report

1. This report has been drawn on the basis of *(substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments (Rules 70.16 and 70.17).)*:

Description, pages:

1-45 as originally filed

Claims, No.:

1-19 as received on 05/01/2001 with letter of 13/12/1999

Drawings, No.:

1-10 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/US99/29666

☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims 5-13,18
	No: Claims 1-4,4-17,19
Inventive step (IS)	Yes: Claims
	No: Claims 1-19
Industrial applicability (IA)	Yes: Claims 1-19
	No: Claims

2. Citations and explanations
see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:
see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/US99/29666

V.

1. In view of the unclarities mentioned below (section VIII.) and as unclear feature cannot be used to distinguish claimed subject-matter from the prior art, the subject-matter of claims 1-4, 14-17 and 19 must be considered to lack novelty in view of

D2a: JP 10 128106 A (TOSOH CORP), 19 May 1998 (1998-05-19)

D2: DATABASE WPI Section Ch, Week 199830 Derwent Publications Ltd.,
London, GB; Class E36, AN 1998-341398 XP002133401

D2b: Patent Abstracts of Japan of D2a

D2c: Computer translation of D2a

D2a discloses an adsorbent for the separation of oxygen by pressure swing adsorption, selectively adsorbing nitrogen from air. The adsorbent comprises a zeolite X exchanged with 80 to 88% lithium and 1 to 5% Cs, Rb, K, Tl or Ag. The Japanese application document D2a (a computer translation of D2a (D2c) is annexed to this report) discloses on page 6 in the tables 1 and 2 lithium, silver exchanged zeolite X, having a silver cation content of 2 and 3 %. The adsorbents of D2a are prepared by a similar process as claimed in claim 16 (See D2c, page 3, [0055] - [0059]). Therefore, it appears implicit that the adsorbent of D2a has the same properties as the claimed one (See PCT International Preliminary Examination Guidelines Chapter IV.-7.5). For these reasons D2a is considered to anticipate the subject-matter of claims 1-4, 14-17, 19.

2. US-A-5 417 957 (D1) discloses an adsorbent for separating nitrogen from gas mixtures containing nitrogen and less strongly adsorbed components such as oxygen, argon etc. (abstract). The adsorbent comprises zeolite X or LSX with between 70%-90% lithium and 5 to 95%, preferably 10%-30% of a second ion. The second ion can be copper. (claims 1, 4- 7). The zeolite can be exchanged sequentially, i.e. firstly exchanging with lithium and then exchanging with the second ion (column 4, lines 22-30). Before use in gas separation the adsorbents is heat treated in a flow of a non-reactive purge gas at between 300 and 650°C. (column 5, lines 35-47).

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/US99/29666

D1 does not disclose copper in a +1 valence state or a partially metallic copper, therefore, the subject-matter of claims 8-13 and 18 is novel over D1.

The subject-matter of claims 5-6 is novel over D2a, because D2a does not disclose an absorbent having less sodium than silver.

3. The subject-matter of claims 5-13 and 18 does not involve an inventive step.

No effect has been demonstrated with respect to valence state of copper or silver in the adsorbent. As long as no technical effect has been related and convincingly demonstrated to this difference, it must be considered as lacking an inventive step.

Further, it is not recognizable which effect is obtainable if the amount of sodium is less than silver. In absence of an effect which is related to the surplus of silver to sodium, no inventive step can be acknowledged therefor.

VII.

1. The units "atmospheres", "cal" employed throughout the description are not additionally expressed in terms of the units stipulated by Rule 10.1(a) PCT.
2. "Incorporation by reference" as made in the description, page 6,31 is not acceptable. If matter in a document referred to is essential to the disclosure of the application, it has to be incorporated into the description, if a document referred to is not essential to the disclosure of the application, then such incorporation by reference shall be deleted, because the description shall be self-contained, i.e., capable of being understood without reference to any other document (see PCT Guidelines II.4.17).
3. The description has not been brought in conformity with the claims as required by Rule 5.1(a)(iii) PCT.

The relevant background art disclosed in the documents D1 and D2 has not been

be mentioned in the description (Rule 5.1(a)(ii) PCT).

VIII.

1. The term "in the form of dispersed clusters" is regarded as not sufficiently clear in order to distinguish the claimed subject-matter from the prior art.
It is not clear from the description how to exactly determine the presence of silver or copper clusters in lithium zeolite X, thus the skilled person has not been enabled to determine when a silver or copper containing zeolite comprises silver or copper clusters.
2. Independent claims stipulate that the amount of M^{1+} shall be up to 10 % of the cation sites. As the number of cation sites per unit cell in X zeolites is 96, the atomic units stipulated in dependent claims 3-4, 6 and 13 of 10 or more are outside the 10% upper limit of the independent claims. This inconsistency between the independent and the dependent claims renders the scope of protection unclear, and is thus not acceptable under Article 6 PCT.
3. The term "about" used in claims 1,6,13,14, 16 and 17 renders the corresponding ranges vague and unclear and leaves the reader in doubt as to the extent of protection, contrary to the clarity requirement of Article 6 PCT (see PCT Preliminary Examination Guidelines, Chapter III, 4.5a).

REPLACED BY
ART 34 AND 71PCT/US99/29666
28 JUN 2001

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What Is Claimed Is:

1. A composition comprising lithium (Li) and metal (M) cation exchanged zeolite where said cation exchanged zeolite is selected from the group consisting of $\text{Li}_x\text{M}_y\text{X}$ zeolite, $\text{Li}_x\text{M}_y\text{LSX}$ zeolite and where said metal (M) is silver or copper and is in the form of dispersed clusters, x is greater than y , the sum of $x + y$ is less than or equal to the number of cation sites of said zeolite, and y is greater than zero.
2. The composition of claim 1 wherein M is silver presented in an atomic amount corresponding to up to about 20% of the cation sites.
3. The composition of claim 1 wherein M is silver presented in an atomic amount corresponding to up to about 10% of the cation sites.
4. The composition of claim 1 wherein the total number of said cation sites is 96, and Y is up to 20.
5. The composition of claim 1 wherein the total number of said cation sites is 96 and Y is up to 10.
6. The composition of claim 1 which is cation exchanged sodium zeolite where sodium is present in an atomic amount less than said silver.
7. The composition of claim 6 wherein the total number of cation sites is 96, lithium is present in an atomic amount greater than 70 and less than 96 atomic units, silver is present in an atomic amount greater than

0 and up to about 20 atomic units, and sodium is present in an atomic amount less than silver.

8. The composition of claim 1 wherein said clusters consist of partially metallic silver.

9. The composition of claim 8 wherein said clusters consist of n atoms of metal (M) collectively having a charge represented by the value $n-1$.

10. The composition of claim 9 wherein said clusters consist of 3 atoms of metal (M) collectively having a +2 charge, or 6 atoms of metal (M) collectively having a +5 charge.

11. The composition of claim 1 wherein said clusters consist of one selected from the group consisting of partially metallic copper and partially metallic silver.

12. The composition of claim 1 wherein M is copper present in atomic amount corresponding to up to about 20% of the cation sites.

13. The composition of claim 1 wherein M is copper present in an atomic amount corresponding to up to about 10% of the cation sites.

14. The composition of claim 1 which is cation exchanged sodium zeolite where sodium is present in an atomic amount less than said copper.

15. The composition of claim 14 wherein the total number of cation sites is 96, lithium is present in

an atomic amount greater than 70 and less than 96 atomic units, copper is present in an atomic amount greater than 0 and up to about 20 atomic units, and sodium is present in an atomic amount less than copper.

16. A process for selectively adsorbing nitrogen from a gas mixture thereof which comprises contacting said gas mixture with an adsorbent which comprises lithium (Li) and metal (M) cation exchanged zeolite where said zeolite is selected from the group consisting of Li_xM_y X zeolite and Li_xM_y LSX zeolite, and where said metal (M) is silver or copper and is in the form of dispersed clusters, x is greater than y, the sum of x+y is less than or equal to the cation sites of said zeolite, and y is greater than 0.

17. The process of claim 16 wherein said zeolite is a lithium and silver exchanged sodium zeolite, said method further comprising contacting said gaseous mixture with said zeolite at a selected temperature and pressure, thereby producing a non-adsorbed component and a nitrogen-rich adsorbed component; and changing at least one of said pressure and temperature to thereby release said nitrogen-rich component from said adsorbent.

18. A process for preparing a composition comprising lithium and metal (M) cation exchanged zeolite where M is in the form of dispersed clusters associated with a plurality of said cation exchanged sites, said method comprising the steps of:

- a. providing a sodium zeolite selected from the group consisting of Na-X zeolite and Na-LSX zeolite;
- b. exchanging a plurality of Na^{1+} ions with Li^{1+} ions;

c. exchanging a portion of said Li^{1+} ions with M^{1+} ions;

d. heat treating the M^{1+} exchanged zeolite of step (c) at a temperature of greater than about 400 degrees centigrade in a non-oxidizing atmosphere to reduce a portion of said M^{1+} ions to M^0 , thereby forming said dispersed clusters.

19. The process of claim 18 wherein in step (c) M^{1+} is Ag^{1+} , and step (d) is conducted at a temperature in a range of about 450° to about 500°C .

20. The process of claim 18 wherein M^{1+} is Cu^{+1} and step (c) is conducted by first exchanging Li^{1+} ions with Cu^{2+} ions and then reducing said Cu^{2+} ions to Cu^{1+} ions.

21. The process of claim 18 wherein in step (d) the non-oxidizing atmosphere is an inert atmosphere, reducing atmosphere, or a vacuum.

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference UM-1626/PCT	FOR FURTHER ACTION <small>see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.</small>	
International application No. PCT/US 99/ 29666	International filing date (day/month/year) 13/12/1999	(Earliest) Priority Date (day/month/year) 30/12/1998
Applicant THE REGENTS OF THE UNIVERSITY OF MICHIGAN et al.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

a. With regard to the language, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international search was carried out on the basis of the sequence listing:

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

2. ☐ Certain claims were found unsearchable (See Box I).

3. ☐ Unity of invention is lacking (see Box II).

4. With regard to the title,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the abstract,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the drawings to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

☒ None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No.

/US 99/29666

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01J20/18 B01D53/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01J B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 417 957 A (C.G. COE) 23 May 1995 (1995-05-23) column 3, line 62 - column 4, line 42 column 5, line 10 - line 46 column 6, line 53 - line 55 ---	1, 4, 5, 11-16, 18, 21
A	DATABASE WPI Section Ch, Week 199830 Derwent Publications Ltd., London, GB; Class E36, AN 1998-341398 XP002133401 & JP 10 128106 A (TOSOH CORP), 19 May 1998 (1998-05-19) abstract --- -/-	1-8, 16, 17

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

17 March 2000

Date of mailing of the international search report

11/04/2000

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Hilgenga, K

INTERNATIONAL SEARCH REPORT

International Application No

US 99/29666

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 937 750 A (UNION CARBIDE CORPORATION) page 2, line 49 - line 100 page 3; examples II,VI	1,18,21
A	US 3 626 020 A (R.W. NEUZIL) 7 December 1971 (1971-12-07) column 3, line 40 - line 44; claim 13	
A	GB 2 302 824 A (INSTITUT FRANCAIS DU PETROLE) 5 February 1997 (1997-02-05)	
A	DATABASE WPI Section Ch, Week 198421 Derwent Publications Ltd., London, GB; Class E36, AN 1984-130101 XP002133402 & JP 59 064510 A (TOYO SODA MFG CO LTD), 12 April 1984 (1984-04-12) abstract	
A	DATABASE WPI Section Ch, Week 199825 Derwent Publications Ltd., London, GB; Class E36, AN 1998-280288 XP002133403 & JP 10 095612 A (NIPPON SANSEI CORP), 14 April 1998 (1998-04-14) abstract	
P,A	EP 0 893 157 A (CECA S.A.) 27 January 1999 (1999-01-27) claims 1,6	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/29666

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5417957 A	23-05-1995	US 5258058 A	02-11-1993
		BR 9303992 A	12-04-1994
		CA 2107144 A	06-04-1994
		CN 1087553 A, B	08-06-1994
		CN 1148568 A	30-04-1997
		EP 0591919 A	13-04-1994
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GB 2302824 A	05-02-1997	FR 2735992 A	03-01-1997
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		IT MI961325 A	29-12-1997
JP 59064510 A	12-04-1984	NONE	
JP 10095612 A	14-04-1998	NONE	
EP 893157 A	27-01-1999	FR 2766476 A	29-01-1999
		CA 2242621 A	22-01-1999
		CN 1211468 A	24-03-1999
		JP 11076810 A	23-03-1999

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : B01J 20/18, B01D 53/04	A1	(11) International Publication Number: WO 00/40332 (43) International Publication Date: 13 July 2000 (13.07.00)
(21) International Application Number: PCT/US99/29666 (22) International Filing Date: 13 December 1999 (13.12.99) (30) Priority Data: 60/114,371 30 December 1998 (30.12.98) US (63) Related by Continuation (CON) or Continuation-in-Part (CIP) to Earlier Application US 60/114,371 (CON) Filed on 30 December 1998 (30.12.98) (71) Applicant (for all designated States except US): THE REGENTS OF THE UNIVERSITY OF MICHIGAN [US/US]; Technology Management Office, The University of Michigan, Wolverine Tower, Room 2071, 3003 South State Street, Ann Arbor, MI 48109-1280 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): YANG, Ralph, T. [US/US]; 2627 Pin Oak Drive, Ann Arbor, MI 48103 (US). HUTSON, Nick, D. [US/US]; 1139 Wendy Court, Ann Arbor, MI 48103 (US).	(74) Agents: DESCHERE, Linda, M. et al.; Young & Basile, P.C., Suite 624, 3001 West Big Beaver Road, Troy, MI 48084-3107 (US). (81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>	
(54) Title: LITHIUM-BASED ZEOLITES CONTAINING SILVER AND COPPER AND USE THEREOF FOR SELECTIVE ADSORPTION (57) Abstract The invention provides new methods for separating nitrogen from a mixture. The invention provides adsorbents specifically for accomplishing nitrogen separation. The adsorbents and separation methods are particularly useful for the selective adsorption of nitrogen from air. In one aspect, the adsorbent comprises an ion exchange zeolite X and preferably zeolite LSX (low silica zeolite X). The zeolite is most preferably a lithium-based zeolite. Further, the zeolite has exchangeable cationic sites, with silver cation or copper cation occupying at least some of the exchangeable cationic sites. The Ag/Cu exchanged zeolite is heat-treated under specific conditions as per the invention. The presence of the silver cation or copper cation at any of the sites will provide an improvement over the non-exchanged zeolite.		

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**LITHIUM-BASED ZEOLITES CONTAINING SILVER AND
COPPER AND USE THEREOF FOR SELECTIVE ADSORPTION**

Field of the Invention

5 This invention relates to a process and adsorbents for selective adsorption of a gas component, and particularly, selective adsorption of nitrogen.

Background of the Invention

10 The separation of air for the production of nitrogen and oxygen is a very important operation in the chemical processing industry. Historically, this separation has been done predominately by cryogenic distillation; though, as adsorption systems have become more efficient and new, more effective sorbents have been
15 synthesized, separation by adsorption processes (e.g., pressure swing adsorption (PSA), and vacuum swing adsorption (VSA)) have become increasingly competitive and are already favorable for small-to-medium scale operations. Currently, approximately 20% of air
20 separations are accomplished using adsorption technologies.

 Since their introduction in the late 1950's, synthetic zeolites have been used in numerous applications such as catalysis, ion exchange, drying, and
25 separation by selective adsorption. In the separation of air, zeolites of type A and X have typically been used. (See U.S. Patent No. 5,551,257, Jain). The A and X type zeolites are composed of silica and alumina tetrahedra

which are joined together to form the truncated octahedral or sodalite structure. These sodalite units are connected with tertiary units to form the structured zeolite unit cell. While the SiO_2 groups are
5 electroneutral, the AlO_2 groups are not, and thus introduce a negative charge to the structure which is offset by the presence of a charge compensating, non-framework cation (e.g., Na^+ , Li^+ , Ca^{2+}). Type X zeolites contain between 77 and 96 Al per unit cell. The unit
10 cell, including cation sites, for the X zeolite is shown in **Figure 1**.

The extra-framework cations in the zeolite are largely responsible for the nitrogen selectivity of these materials. These zeolites adsorb nitrogen preferentially
15 to oxygen (usually at a ratio of about 4:1) due primarily to the interactions between the charge compensating cations of the zeolite and the quadruple moment of the adsorbing gas (N_2 or O_2). The quadruple moment of N_2 is approximately four times that of O_2 . Because the extra-
20 framework cations so significantly influence the adsorption properties of the zeolites, numerous attempts have been made to optimize these properties by (1) increasing the number of cation sites (the cation exchange capacity, CEC) by creating zeolites with high
25 aluminum content, and (2) by synthesizing zeolites containing various alkaline, alkaline earth, and combinations of these cations.

Low silica X-type zeolite (LSX) is known. This material is an aluminum saturated X-type zeolite with a
30 silica-to-alumina ratio of 2.0 (or $\text{Si}/\text{Al} = 1.0$). Commercial X-zeolite, which is typically available as the Na^+ form (known commercially as 13X), is not aluminum

saturated and contains 86 aluminum atoms per unit cell, while the low silica X zeolite contains 96 aluminum atoms per unit cell.

Li⁺ is among the strongest cations, with
5 respect to its interaction with N₂, its use was greatly increased with two recent advances. First, it was found that Li⁺ ion-exchange in X-type zeolite must exceed an approximate 70% threshold before the Li⁺ has any affect on the adsorption properties of the material (U.S. Patent
10 No. 4,859,217, Chao). Second, a significant increase in the N₂ adsorption capacity was seen in Li⁺ ion exchanged low silica X-type zeolites over that of the typical commercial zeolites (Si/Al = 1.25). Because of these advances, Li-X (Si/Al = 1.0) is now the best sorbent in
15 industrial use for separation of air by adsorption processes (U.S. Patent No. 5,268,023, Kirner; U.S. Patent No. 5,554,208, Mullhaupt).

Sicar et al., U.S. Patent No. 4,557,736 and Coe et al., U.S. Patent No. 4,481,018 reported the use of a
20 binary exchanged X-zeolite having lithium and calcium and/or lithium and strontium ions in a ratio of 5% to 50% calcium and/or strontium and 50% to 95% lithium. This zeolite provided for enhanced nitrogen adsorption over those of the Na-X, Li-X and Ca-X zeolites. They also
25 reported the use of mixed ion-exchanged A and X zeolites with lithium and an alkaline earth metal (e.g., Ca²⁺, Sr²⁺). In this case the zeolite contained lithium and the alkaline earth cations in a mixture of 10% to 70% alkaline earth and 30% to 90% lithium. These mixed
30 cation zeolites provide good adsorption capacity and good thermal stability. However, the cost of separation still remains high. Therefore, there remains the need for

improved methods and adsorbents to effectively and economically separate nitrogen from a gaseous mixture.

Summary of the Invention

The invention provides new methods for separating nitrogen from a mixture. The invention provides adsorbents specifically for accomplishing nitrogen separation. The adsorbents and separation methods are particularly useful for the selective adsorption of nitrogen from air. In one aspect, the adsorbent comprises an ion exchange zeolite X and preferably zeolite LSX (low silica zeolite X). The zeolite is most preferably a lithium-based zeolite. Further, the zeolite has exchangeable cationic sites, with silver cation or copper cation occupying at least some of the exchangeable cationic sites. The presence of the silver cation or copper cation at any of the sites will provide an improvement over the non-exchanged zeolite. Therefore, the minimum amount of silver cation or copper cation is greater than zero. The inclusion of silver cation and/or copper cation at the exchangeable cationic sites provides such an improvement in strength of adsorption of nitrogen, that any amount is helpful. However, consideration is given to the strength of such adsorbent capacity when optimizing the amount, in view of subsequent desorption. Since Ag^+ and Cu^+ strongly hold nitrogen, it is desirable that the amount of such cation be up to about 20% of the exchangeable cationic sites. It is preferred that the silver or copper cation occupy about 10% of the exchangeable cationic sites. Such optimization leads to a good balance between strength of adsorption and facilitating subsequent desorption. Therefore, it is evident that not all of the ion exchangeable cationic sites of the zeolite will contain copper or silver and preferably less than half of such sites will be so exchanged.

Zeolites are known and have been used as adsorbents due to their selectivity. Crystalline zeolite Y, zeolite A, and zeolite X are examples and are described in U.S. Patent Nos. 3,130,007; 2,882,243; 3,992,471; and 2,882,244; each of which is incorporated by reference in its entirety. Type 5A zeolite, and type 13X zeolite are described for nitrogen adsorption in U.S. Patent No. 5,551,257, also incorporated herein by reference in its entirety. Low silica X zeolite (LSX) having Si/Al ratio less than or equal to 1.25, desirably less than or equal to 1.2, and preferably about 1, is described in U.S. Patent No. 5,268,023. Each of the aforementioned patents is incorporated herein by reference in its entirety. Consistent with the features described in these patents, zeolite characteristics are also described in the reference book entitled "Gas Separation by Adsorption Processes" by R.T. Yang (1987 Butterworth Publishers). To the extent that zeolite characteristics are pertinent to the present invention, they will be described further hereinbelow.

In the practice of the invention, the important characteristic desired is imparted by the presence of silver and/or copper cation in a zeolite which has been previously exchanged to provide a lithium X zeolite or a lithium LSX zeolite. The desirable X zeolite has a silicon to aluminum ratio (Si/Al) of about 1 to about 1.3. The more desirable lithium LSX has the preferred silicon to aluminum ratio of 1.0. Therefore, the adsorbents of the invention are essentially silver or copper ion exchanged Li^+ zeolites. The presence of the silver cation or the presence of the copper cation in combination with the lithium cation provides the desired characteristic for improved nitrogen adsorption.

However, the zeolite may also include minor amounts of other commonly found cations which occur in zeolite including, but not limited to besides lithium, potassium, sodium, rubidium, caesium, and mixtures thereof which are
5 alkali metal cations; and alkaline earth metal cations beryllium, magnesium, calcium, strontium, barium, and mixtures thereof. The presence of a trivalent cation is also possible, however, such is not preferred in order to provide available sites for occupancy by the preferred
10 silver, copper, and lithium.

In another aspect, the adsorbents of the invention are used in a method for separating nitrogen from a gaseous air mixture, by accomplishing adsorption at a first select pressure and temperature and then
15 accomplishing release or desorption by changing at least one of the pressure and temperature. Preferential adsorption of nitrogen is preferably achieved by pressure swing adsorption. Conveniently, this may be carried out and is preferably carried out at about ambient room
20 temperature conditions. Therefore, special temperature treatment is not required. In the pressure swing process, the preferred range for adsorption is about 1 to about 10 atmospheres, and the preferred range for desorption is about 0.2 atmospheres to about 1
25 atmosphere.

In the process for preparing the zeolites of the invention, first lithium zeolites are prepared by ion exchange using lithium chloride. Then these lithium-zeolites were used to prepare Li_xAg_y -zeolites and Li_xCu_y -
30 zeolites. For convenience, these will be referred to as mixed cation zeolites containing lithium, and transition metal capable of a +1 valence state (targeted metal ion).

The preparation of the Li_xAg_y-zeolites is exemplary and is accomplished by ion exchange of a Li-zeolite, prepared as described earlier, with a solution of silver nitrate. The copper ion exchange is accomplished in a comparable manner. Ion exchange of zeolite is easily accomplished by mixing the zeolite in an aqueous solution of metal salt. The metal of the salt is the metal to be exchanged into the cationic site. The concentration of the solution is varied according to the desired level of ion exchange. The ion exchanged zeolite is then removed by filtration from the aqueous solution and washed free of the soluble salts. The Cu-zeolites of the invention are prepared by ion exchanging with a copper salt solution preferably copper chloride or copper nitrate, followed by reduction of any copper +2 to copper +1.

After the incorporation of the targeted metal ion, the mixed cation material is dried at room temperature and atmospheric conditions. Dehydration in vacuo may follow later, and prior to use and/or analysis. Zeolites have a strong affinity for water; and some molecules are tenaciously held. The presence of water in the zeolite affects measurement. In the process of the present invention, specific conditions for heat treatment are used beyond the treatment required for mere dehydration. In the present invention, specific heat treatment is used to optimize performance of the mixed cation zeolite of the invention. The heat treatment, after ion exchange, of the mixed cation zeolite is above a minimum temperature of approximately 400°C. A temperature of 400°C or greater is required in order to form crystal clusters of silver and/or copper. The upper limit to the heat treat temperature is 700°C; and preferably is below 700°C, as this is determined to be

the point at which destruction of the zeolite itself occurs. The heat treatment is able to be accomplished in air, in vacuum, in inert atmosphere such as argon, nitrogen, or in reducing atmosphere. Desirably, the heat treatment is in a non-oxidizing atmosphere such as in vacuo, in inert atmosphere, or reducing atmosphere. An air atmosphere is less desirable. The non-oxidizing atmosphere is selected to produce partially metallic clusters, and provide the cluster formation and character of the zeolite product described herein. Here inert means inert with respect to the metal ions, cluster formation and character of the zeolite. Thus, the atmosphere needs to be unreactive with the zeolite, and not interfere with formation of desired ion clusters. Treatment temperatures on the order of 20 to 30 minutes are thought to be a minimum. There is no real maximum to the duration of heat treatment time and such time has been extended to 5 hours without any difficulty. Typical heat treatment time varies from about 1 to about 4 hours; and more typically 1 to 2 hours.

The preferred lithium content of the zeolite is such that, of the available cationic sites, 70% or more and preferably 80% or more of such sites contain lithium. It is preferred that the proportion of cationic sites occupied by the silver and/or copper be up to about 10%, although up to about 20% is workable as described earlier. Compositions as described hereinbelow were prepared and found to be operable for a variety of ranges including 0.5 to 5% of the cationic sites occupied by silver; over 88% of cationic sites occupied by lithium; and with other alkali and alkaline earth metals constituting the balance. The compositions contain the aforesaid metallic clusters where the metal (M), copper

or silver, is desirably partially metallic. This is exemplified by clusters of n number of metal atoms collectively having a charge represented by $n-1$. This is expressed as $M_n^{(n-1)}$ where n is 2 or more, and examples are
5 Ag_3^{2+} and Ag_6^{5+} .

The invention provides substantial advantages over conventional methods for separating nitrogen from an air mixture due to the effective and economical processes and adsorbents provided by the invention.

10 Objects, features, and advantages of the invention include an improved method for separating nitrogen from a gaseous mixture, and particularly for separating nitrogen from air. Another object is to provide new adsorbents used in such new separation
15 method.

 These and other objects, features, and advantages will become apparent from the following description of the preferred embodiment, claims, and accompanying drawings.

Brief Description of the Drawings

Figure 1 shows unit cell of faujasite-type (X and Y) zeolites including cation sites.

Figure 2 shows adsorption isotherms for N₂, O₂ and Ar measured at 25°C for Li₉₆-X-1.0 Si/Al zeolite dehydrated in vacuo at 350°C. This nominal Li₉₆-X-1.0 is Li_{94.5}Na_{1.5}-X-1.0.

Figure 3 shows N₂ adsorption isotherms, measured at 25°C for (a) nominal Li₈₆X-1.25 Si/Al which is Li₇₇Na₉X-1.25 and (b) nominal Li₉₆-X-1.0 Si/Al which is Li_{94.5}Na_{1.5}-X-1.0. Both materials were dehydrated in vacuo at 350°C.

Figure 4 shows adsorption isotherms measured at 25°C for N₂, O₂ and Ar on nominal Ag₉₆-X-1.0 Si/Al zeolite which is Ag_{95.7}Na_{0.3}-X-1.0 dehydrated in vacuo at 450°C.

Figure 5 shows N₂ adsorption isotherms, measured at 25°C, for (a) nominal Ag₈₆-X-1.25 Si/Al which is Ag_{85.7}Na_{0.3}-X-1.25 and (b) nominal Ag₉₆-X-1.0 Si/Al which is Li_{95.7}Na_{0.3}-X-1.0. Both materials were dehydrated in vacuo at 450°C.

Figure 6 shows N₂ adsorption isotherm, measured at 25°C, for Li_xAg_y-X-1.0 Si/Al (Li_xAg_y-X-1.0) zeolites dehydrated in vacuo at 450°C. This shows the addition of increasing amounts of Ag results in a change in the general aspect of isotherm toward that of the fully Ag⁺-exchanged material.

Figure 7 shows N_2 adsorption isotherm, measured at 25°C, for nominal $Ag_{96}-X-1.0$ Si/Al which is $Ag_{95.7}Na_{0.3}-X-1.0$ (left) and nominal $Li_{96}-X-1.0$ Si/Al which is $Li_{94.5}Na_{1.5}-X-1.0$ (right). The materials were dehydrated in vacuo at (a) 350°C and (b) 450°C.

Figure 8 shows plots of $\ln(P)$ vs $1/T$ at different coverages for nominal $Li_{96}-X-1.0$ Si/Al which is $Li_{94.5}Na_{1.5}-X-1.0$ (left) and nominal $Li_{95}Ag_1-X-1.0$ Si/Al which is $Li_{94.2}Na_{0.7}Ag_{1.1}-X-1.0$ (right).

Figure 9 shows isosteric heats of adsorption of N_2 for nominal $Li_{96}-X-1.0$ Si/Al which is $Li_{94.5}Na_{1.5}-X-1.0$ and nominal $Li_{95}Ag_1-X-1.0$ Si/Al which is $Li_{94.2}Na_{0.7}Ag_{1.1}-X-1.0$.

Figure 10 shows N_2 and O_2 isotherms for nominal $Li_{95}Ag_1-X-1.0$ Si/Al which is $Li_{94.2}Na_{0.7}Ag_{1.1}-X-1.0$ dehydrated in vacuo at 450°C and for nominal $Li_{96}-X-1.0$ Si/Al which is $Li_{94.5}Na_{1.5}-X-1.0$ dehydrated in vacuo at 350°C. All isotherms were measured at 25°C.

Detailed Description of the Preferred Embodiments

In one aspect, the invention provides type X zeolites comprising varying mixtures of Li and one or more transition metal having +1 valence state and selected from Ag (silver), Cu (copper), and mixtures thereof. The invention is demonstrated using silver. The experimental results show that even very small amounts of the +1 transition metal leads to beneficial results. Small amounts of Ag on the order of less than 5 Ag per unit cell (UC) were very effective. The addition of very small amounts of Ag and the proper dehydration conditions resulted in the formation of silver clusters and enhanced adsorptive characteristics and increased energetic heterogeneity as compared to those of the fully exchanged Li-zeolites. The performance for air separation by the best of these sorbents, containing, on the average, only one Ag per unit cell, was compared to that of the fully Li⁺-exchanged zeolite using a standard PSA cycle by numerical simulation. The results show that the new sorbent provides a significantly higher (>10%) product throughput, at the same product purity and recovery, when compared to that of the fully Li⁺-exchanged zeolite.

Silver has been found to have very strong effects on the adsorption characteristics of zeolites. The synthesis of a mixed lithium-silver (80/20) ion-exchanged X-type zeolite (Si/Al = 1.25 with approximately 17 Ag⁺ per unit cell), has been identified for possible superior properties for air separation. This sorbent utilized the very strong adsorptive properties of the Ag⁺ ion which provided for increased capacity over that of the Li-X while maintaining some degree of the

advantageous isotherm linearity that is seen with Li-X. *Ab initio* molecular orbital calculations showed the adsorption of nitrogen was enhanced by weak chemical interaction (through a classical π -complexation bond) with the Ag^+ cation on the zeolite framework.

Transition metal ions were reduced in zeolites for the purpose of forming highly dispersed metallic clusters for use as catalysts. This generally involved treatment at elevated temperatures and/or in reducing atmospheres (e.g., sodium vapor, hydrogen gas, carbon monoxide gas). However, color changes upon vacuum dehydration of silver-exchanged A-type zeolites were found to be related to the formation of metallic clusters within the sodalite cage or the 6-prism of the zeolite. Using volumetric sorption techniques and temperature programmed desorption, it was possible to relate these color changes to an autoreductive process involving framework oxygens. Autoreduction is the reduction of the transition metal ion and the oxidation of water or lattice oxygen; this has been observed for both Ag^+ and Cu^{2+} ions in zeolites A, X and Y, and has been shown to take place by two mechanisms in two clearly defined temperature regions: (i) autoreduction in the presence of zeolite water (25–250°C) (See Equation 1; and (ii) autoreduction by oxygen from the zeolite lattice (127–380°C) (See Equation 2).

While not wishing to be held to any particular theory, in one aspect the formation of octahedral hexasilver metal clusters stabilized by coordination to six silver ions ($(\text{Ag}^+)_6(\text{Ag}^0)_6$) is proposed from x-ray structural determinations of a dehydrated silver-exchanged zeolite A. In another aspect, it is suggested

that the formation of such large metal clusters is improbable since color changes are seen even at low temperatures and low silver loadings where extensive migration of neutral silver atoms and subsequent sintering into Ag_6 metal clusters is highly unlikely. In still another aspect, based on structural studies of Ag-A zeolites, the formation of linear $(\text{Ag}_3)^{2+}$ charged clusters ($\text{Ag}^+-\text{Ag}^0-\text{Ag}^+$) is thought to occur upon thermal dehydration of the zeolite. Color changes were followed along with concomitant silver cluster formation in A, X, and Y zeolites using x-ray diffraction (XRD) techniques. Here, it was found that the number of clusters increased with framework Al content. It was also noted that in synthetic analogs of the faujasite zeolite (types X and Y), the dehydrated zeolites displayed a yellow color which increased in intensity with the number of clusters, while silver-exchanged A zeolites took a yellow color with dehydration at low temperatures, eventually becoming brick red after treatment at higher temperatures.

The present invention provides type X zeolites containing varying amounts of Li and along with the Li, one or more of Ag and Cu. These materials are heat treated in a way which promotes the formation of intracrystalline silver clusters or copper clusters. The resulting adsorptive characteristics were evaluated with respect to the gases which are of primary interest in the separation of air: N_2 , O_2 and Ar. The performance of the best of these sorbents was compared to that of the fully Li^+ -exchanged zeolite using a numerical simulation of a standard five-step PSA cycle, that is used in industry, and the results are given below.

Experimental Section Materials

Two type-X zeolites, differing only by the Si/Al ratio, were used in this work. These were: (1) X-type zeolite with a Si/Al of 1.0 (Praxair, #16193-42, sometimes referred to as LSX, low silica X-zeolite), and
5 (2) X-type zeolite with a Si/Al of 1.25 (Linde, lot 945084060002). Both of these materials were binderless, hydrated powders.

Helium (99.995%, prepurified), oxygen (99.6%, extra dry), nitrogen (99.998%, prepurified) and argon
10 (99.998%, prepurified) were obtained from Cryogenic Gases. All water used was deionized.

Cation Exchange

Since the sodium form of the zeolite exchanges
15 more readily with most cations in consideration, all zeolites were first ion-exchanged with a solution of sodium chloride in order to convert to the Na⁺ form. A dilute NaOH solution was used to keep the NaCl solution at pH ≈ 9. This helped to prevent hydrolysis and break
20 down of the zeolite crystal structure during the ion-exchange process. The resultant Na-zeolite was then used as the starting material for all other syntheses.

Preparation of Li-Zeolites

The lithium zeolites were prepared by 5 consecutive static ion-exchanges using a 6.3-fold excess (over that necessary for full ion-exchange) of a 2.2 M solution of LiCl. This was done in a 0.01 M solution of
5 LiOH at a pH \approx 9. The lithium ion-exchange solution was heated to a mild boil and then allowed to cool and settle. The solution was decanted, a fresh 6.3X LiCl solution was added, and the procedure was repeated for a
10 total of 5 exchanges. After the final ion-exchange, the material was vacuum filtered and washed with copious amounts of deionized water until no free ions were present in the filter water (i.e., no AgCl precipitation upon treatment with Ag⁺). The resulting lithium
15 exchanged zeolites were dried overnight at 100°C in a conventional oven before being dehydrated *in vacuo* prior to measurement of adsorption isotherms.

Preparation of Ag-Zeolites

The silver zeolites were prepared by 2 consecutive ion-exchanges using a 0.05 M solution of
20 AgNO₃. Each silver solution contained a cation content which was double that required for 100% exchange. The silver ion-exchange solution was heated to a mild boil and immediately allowed to cool and settle. As with the
25 lithium ion-exchange, the solution was decanted, fresh AgNO₃ solution was added, and the procedure was repeated for a total of 2 exchanges. After the second ion-exchange, the material was vacuum filtered and washed with copious amounts of deionized water until no free
30 ions were present in the filter water (i.e., no precipitation upon treatment with Cl⁻). The silver

exchanged materials were dried at room temperature and atmospheric conditions in a dark area. The resulting materials were then stored in a dark area until they were dehydrated *in vacuo* prior to analysis.

5 **Preparation of Li_xAg_y -Zeolites**

The Li_xAg_y -zeolites were prepared by ion exchange of a Li-zeolite (prepared as described above) with a 0.05 M solution of AgNO_3 . This silver solution contained a cation content which was equivalent to the targeted amount. This was possible with silver ion-exchange because the silver cation is quickly and easily exchanged. The silver ion-exchange solution was heated to a mild boil and immediately allowed to cool and settle. The resulting material was vacuum filtered and washed with copious amounts of deionized water. Complete incorporation of the targeted silver ions was verified when no precipitation was observed in the filtered water upon treatment with Cl^- . These mixed cation materials were dried at room temperature and atmospheric conditions in a dark area and were stored in a dark area until they were dehydrated *in vacuo* prior to analysis. The Li_xAg_y -zeolites are more accurately referred to as $\text{Li}_x\text{Na}_y\text{Ag}_z$ -zeolites since ion exchange is rarely exhaustive and there is almost always some residual Na^+ present in the starting Li-zeolite.

Dehydration

Prior to measurement of the adsorption isotherms or uptake rates, it is necessary to dehydrate the zeolite sample. Zeolites have a strong affinity for water; and some molecules are tenaciously held. The

presence of water in the zeolite significantly affects the validity of the adsorption measurement. Prior to analysis, all samples were heated in order to remove water. Differential thermal analysis (DTA) of zeolite X
5 demonstrated a continuous loss of water over a broad range of temperatures, starting at slightly above room temperature up to 350°C with a maximum at about 250°C. Specific dehydration conditions varied from sample to sample and are given for each sample.

10 **Characterization**

The ion-exchanged, mixed LiAgX zeolite samples were analyzed for Ag and Li contents using an inductively coupled plasma mass spectrometer (ICP-MS, Hewlett Packard HP 4500). The samples were first digested in
15 concentrated nitric acid solution at 100°C for 20 minutes. At the end of digestion, the samples were further diluted and filtered. The filtrates were subjected to ICP-MS analyses.

The adsorption isotherms were measured using a
20 static volumetric system (Micrometrics ASAP-2010). Additions of the analysis gas were made at volumes required to achieve a targeted set of pressures. A minimum equilibrium interval of 9 seconds with a tolerance of 5% of the target pressure (or 0.007 atm,
25 whichever was smaller) was used to determine equilibrium for each measurement point. The pressure transducers in the ASAP-2010 are accurate to <0.2% for the pressure range of 0-1 atm. The sample weights were obtained using a digital laboratory balance which is accurate to ± 0.01 g.
30 The isotherm measurements and the samples themselves were found to be highly reproducible.

In addition, the samples were compositionally characterized using neutron activation analysis (NAA) in the research nuclear reactor of the Phoenix Memorial Laboratory at the University of Michigan. The samples were irradiated sequentially for one minute at a core-face location with an average thermal neutron flux of 2×10^{12} n/cm²/s. Two separate gamma-ray spectra were then collected for each sample with a high resolution germanium detector: one after a 13 minute decay to determine the concentrations of Al and Ag, and a second after a 1 hour and 56 minute decay to analyze for Na and K; both were for 500 seconds real time. Four replicates of NBS-SRM-1633a (coal fly ash) and silver foil were used as standard reference materials and check standards. Absorbent parameters and PSA simulation results are described with reference to Tables 1-3. Results of compositional characterization (NAA and ICP-MS) are given in Table 4. The unit cell compositions for those analyzed samples are given in Table 5.

Results and Discussion

All samples are identified according to the type of zeolite, the number of charge compensating cation(s) present in a unit cell, and the Si/Al ratio. For example, Li₈₆-X-1.25 refers to an X-type zeolite with Si/Al = 1.25 which has been fully exchanged to contain 86 Li⁺ cations per unit cell. The sample Li₈₆Ag₁₀-X-1.0 refers to an X-type zeolite with Si/Al = 1.0 which contains 86 Li⁺ and 10 Ag⁺ (or other forms of Ag) per unit cell. The sample Li_{94.2}Na_{0.7}Ag_{1.1}-X-1.0 refers to an X-type zeolite with Si/Al = 1.0 which contains, on average, 94.2 Li⁺, 0.7 Na⁺, and 1.1 Ag⁺ (or other forms of Ag) per unit cell, as determined from the neutron activation (NA)

and ICP-MS analyses. It should be noted that the zeolites herein are referred to for convenience by the nominal amount of Li and Ag substituted for the Na. More precise values are given for each of the zeolites. For example, $\text{Li}_{96}\text{-X-1.0}$ is more precisely $\text{Li}_{94.5}\text{Na}_{1.5}\text{-X-1.0}$, since replacement of the Na by Li is not fully accomplished.

Adsorption Isotherms for Fully Exchanged Li and Ag Zeolites

Figure 2 shows the N_2 , O_2 and Ar adsorption isotherms, measured at 25°C , for $\text{Li}_{96}\text{-X-1.0}$ ($\text{Li}_{94.5}\text{Na}_{1.5}\text{-X-1.0}$) after vacuum dehydration at 350°C . This zeolite was used in adsorptive air separation because of its very high N_2 capacity and very favorable $\text{N}_2:\text{O}_2$ selectivity (approximately 6:1 at 1 atm) as well as its N_2 isotherm linearity. Figure 3 shows the enhancement in the N_2 adsorption capacity for $\text{Li}_{96}\text{-X-1.0}$ ($\text{Li}_{94.5}\text{Na}_{1.5}\text{-X-1.0}$) over that of the $\text{Li}_{86}\text{-X-1.25}$ ($\text{Li}_{77}\text{Na}_9\text{-X-1.25}$).

Figure 4 shows N_2 , O_2 and Ar adsorption isotherms for $\text{Ag}_{96}\text{-X-1.0}$ ($\text{Ag}_{95.7}\text{Na}_{0.3}\text{-X-1.0}$), all measured at 25°C , after vacuum dehydration at 450°C for a minimum of 4 hours. These samples were all initially gray in color, but after vacuum dehydration turned to a deep golden yellow, indicating the formation of silver clusters. Figure 5 shows the enhancement in the N_2 adsorption capacity for $\text{Ag}_{96}\text{-X-1.0}$ ($\text{Ag}_{85.7}\text{Na}_{0.3}\text{-X-1.25}$) over that of the $\text{Ag}_{86}\text{-X-1.25}$ ($\text{Li}_{85.7}\text{Na}_{0.3}\text{-X-1.0}$). While the fully exchanged Ag-zeolites, like their Li-zeolite analogs, have very high N_2 capacity and favorable $\text{N}_2:\text{O}_2$ selectivity, they are not favorable for use in adsorption-based separations. Because of the strong

adsorption of N_2 at low pressure, creating a low pressure "knee" in the adsorption isotherm shown in **Figure 4**, the working capacity (i.e., the ΔQ , the change in the adsorptive capacity from the typically used adsorption pressure of 1.0 to a desorption pressure of 0.33 atm) is very small; and the sorbent must be exposed to very low pressure conditions in order to increase that working capacity.

Some Ag-zeolites are demonstrated to have a selectivity for Ar over O_2 . The present examples and data reveal that the Ag-zeolites which had been dehydrated in vacuo at $350^\circ C$ also showed a selectivity for Ar over O_2 . However, the Ag-zeolites which had been dehydrated in vacuo at $450^\circ C$ had approximately the same adsorption capacity for Ar and O_2 (as shown in **Figure 4**). This is probably due to increased interaction between the charged Ag-clusters and the quadrupole moment of the O_2 molecule (whereas, the Ar has no quadrupole moment).

In **Figure 2**, it can be seen that the comparative lithium exchanged sodium zeolite is highly selective for the absorption of nitrogen and also preferentially absorbs oxygen as compared to argon. This is undesirable for the purification of oxygen since the less selectively absorbed argon will remain with the oxygen product. Turning to **Figure 4**, it can be seen that the silver exchanged sodium zeolite has high selectivity for nitrogen but is not preferentially selective for oxygen as compared to argon. This means that the purified oxygen stream will not be relatively argon rich as compared to the pre-absorbed argon content. The mixed lithium silver zeolite of the present invention is adaptable for selectivity for argon as compared to

oxygen. This means that the lithium silver zeolite of the invention is most favorable for oxygen production because the argon will be removed along with the nitrogen, providing an oxygen stream after absorption which has a smaller fraction of argon. Accordingly, the mixed lithium silver zeolite of the invention is more favorable for oxygen production because it provides absorption of nitrogen without the disadvantage of also being highly selective for absorption of oxygen over argon.

Adsorption Isotherms for Mixed Cation (Li_xAg_y) Zeolites

The N_2 adsorption isotherms, measured at 25°C , for $\text{Li}_x\text{Ag}_y\text{-X-1.0}$ ($\text{Li}_x\text{Ag}_y\text{-X-1.0}$) zeolites, after being vacuum dehydrated at 450°C for a minimum of 4 hours, are shown in **Figure 6**. These zeolites contained varying amounts of Ag per unit cell ranging from zero (i.e., the fully exchanged $\text{Li}_{96}\text{-X-1.0}$ ($\text{Li}_{94.5}\text{Na}_{1.5}\text{-X-1.0}$) sorbent) to 10 (the $\text{Li}_{86}\text{Ag}_{10}\text{-X-1.0}$ sample ($\text{Li}_{73.8}\text{Na}_{1.2}\text{Ag}$)). This plot reveals that the incorporation of only a small amount of silver changes the adsorptive properties as compared to the fully exchanged $\text{Li}_{96}\text{-X-1.0}$. With increasing additions of Ag^+ (and corresponding removal of Li^+) the adsorption isotherms begin to take on more of the characteristics of the fully exchanged $\text{Ag}_{96}\text{-X-1.0}$ ($\text{Ag}_{95.7}\text{Na}_{0.3}\text{-X-1.0}$) material (i.e., the high "knee" at low pressures).

Dehydration and Formation of Ag-clusters

As mentioned earlier, zeolites have a strong affinity for water; and some molecules are held tenaciously. The zeolites must be completely dehydrated prior to measurement of the adsorption isotherms in order to guarantee the validity of the result. Importantly, it was found that the dehydration conditions have a very significant effect on the formation of silver clusters. The atmosphere and temperature of the dehydration were found to be the most important. Figure 7 shows N_2 adsorption isotherms for the fully exchanged Ag_{96} -X-1.0 (left) and the fully exchanged Li_{96} -X-1.0 (right), both after vacuum dehydration at 350°C and 450°C. For the fully exchanged Li zeolite, there was no significant increase in the N_2 capacity (or in the shape of the adsorption isotherm) for the material dehydrated at 450°C over that dehydrated at 350°C. This was expected as the majority of the hydrate was easily removed by 250°C and most tenaciously held water molecules were removed by 350°C. However, the fully exchanged Ag_{96} -X-1.0 sample does show an increase in N_2 capacity after dehydration at 450°C over that of the same sample dehydrated at 350°C. This increase cannot be attributed a loss of water since all but the most tenaciously held water is removed by 350°C; and there is no increase in the N_2 capacity for other zeolite forms (Li^+ , Na^+ , K^+ , etc.) with dehydration at temperatures beyond 350°C. This increase, therefore, was the result of the formation of silver clusters in the zeolite with dehydration at high temperature.

A series of N_2 adsorption isotherms were measured for Ag_{96} -X-1.0 and Li_{86} - Ag_{10} -X-1.0 after partial or full dehydration in vacuum at various temperatures.

The results for both zeolites showed a continual increase in the N₂ adsorption capacity (at 1 atm) with increasing dehydration temperature up to about 450 to about 500°C. Samples which had been dehydrated in vacuum at 550°C and 600°C had N₂ capacities which were considerably lower than those dehydrated in vacuum at the 450 - 500°C range.

It was striking that the ultimate adsorptive characteristics of the silver-containing zeolites were very dependent upon the formation of silver clusters and, therefore, on the dehydration conditions. Best results were obtained when the silver-containing zeolites were dried at room temperature before being completely dehydrated in vacuum at a temperature of at least 450°C, but no greater than 500°C. The results also showed that the zeolites are most preferably held at the dehydration temperature for a minimum of 4 hours.

Heat of Adsorption and Energetic Heterogeneity

Heterogeneity in zeolites may result from a number of causes. The existence of different cation sites is one of them. If the intra-crystalline cation population is mixed, sites in the vicinity of a cation will differ for each cation whether or not they occupy equivalent crystallographic positions. Further, in a mixed cation population the proportion of one cation to another may vary from one cavity to another so that the behavior of the cavities as multiple sorption sites may vary throughout the crystal.

The presence of energetic heterogeneity of a sorbent can be determined by plotting the isotheric heat of adsorption versus the amount adsorbed. Energetic

heterogeneity of the system will result in a decrease in the isotheric heat of adsorption as the amount sorbed increases. For small uptakes, the isotheric heat may decrease rather strongly with the amount adsorbed. This would be an indication that there are some local intracrystalline positions where the guest molecules are preferentially sorbed more strongly than in the rest of the intracrystalline volume. At intermediate uptakes, the slope of this plot will usually decrease and become nearly constant.

The measurement of adsorption isotherms at different temperatures permits the calculation of the heat of adsorption as a function of surface coverage. When experimental data are reported as a set of adsorption isotherms for a particular gas-adsorbent system, the differential isotheric heat of adsorption is determinable. The isotheric heat of adsorption is calculated from a series of isotherms by application of the Clausius-Clapeyron equation given below as Equation (3).

Using the data from nitrogen and oxygen adsorption isotherms measured at 50°C, 25°C, and 0°C, the isotheric heats of adsorption were determined by evaluating the slope of a plot of $\ln(P)$ versus $(1/T)$ at several coverages. The plots of $\ln(P_{N_2})$ versus $(1/T)$ at several coverages for $Li_{9.6}-X-1.0$ and $Li_{9.5}Ag_1-X-1.0$ ($Li_{9.4.2}Na_{0.7}Ag_{1.1}-X-1.0$) are shown in **Figure 8**. The isotheric heats of adsorption at different coverages were calculated for each of these materials and are shown in **Figure 9**. A similar analysis was also done for the oxygen and argon data, but these results are not shown. From the plots of the heats of nitrogen adsorption, shown

in **Figure 9**, one can see that the isotheric heat of adsorption for N_2 on $Li_{95}Ag_1-X-1.0$ is quite high (≈ 8 kcal/mol) at low coverages, but immediately drops sharply to become nearly horizontal. This indicates the presence of local intracrystalline sites where the N_2 is preferentially sorbed more strongly than at other sites within the intracrystalline volume. A comparison with the same plot of the isotheric heat of adsorption for N_2 on $Li_{96}-X-1.0$, which is essentially horizontal, shows that the energetic heterogeneity of the $Li_{95}Ag_1-LSX$ zeolite is due entirely to the incorporation of the one Ag per unit cell. The plots of the heats of adsorption for O_2 and Ar were horizontal with coverage, indicating the interaction between the silver clusters and these guest molecules was much less than with the N_2 . The approximately constant heat of adsorption with increasing coverage for the $Li_{96}-X-1.0$ is consistent with expected results, and likely indicates an energetically homogeneous surface.

Cation Site Location

For the X zeolites, the cation site designations are conventionally designated as SI (the center of the hexagonal prism), SI' (opposite SI but located in the cubooctahedron), SII (single six-ring in the supercage), SII' (opposite SII but inside the cubooctahedron), and SIII (near the four-ring windows in the supercage).

Several studies have been undertaken in order to locate extra framework Li^+ cations in X, Y and A zeolites using solid state NMR and neutron diffraction methods. It was found that the Li^+ ions fully occupy all

32 SI' sites and all 32 SII sites. The SIII sites were then occupied with the remaining Li⁺ ions, 22 for Li₈₆-X-1.25 and 32 for Li₉₆-X-1.0. No occupancy of the SI sites was observed. One report noted an occupancy "threshold" of 64 Li cations. Mixed Li_xNa_y-X zeolites which contained Li⁺ less than this threshold amount did not show any increase in the N₂ adsorption capacity over that of the fully Na⁺-exchanged samples. This indicated that only those Li⁺ ions located in the SIII cation sites were interacting with the N₂ molecules. This result is interesting because, even though the SI and SI' sites are sterically inaccessible to the N₂ molecules, the SII sites are not; while other cations, such as Ca⁺², do interact with N₂ when located in the SII positions.

In order to identify the location of Ag⁺ ions and Ag-clusters, typically x-ray diffraction methods and far-infrared spectroscopy were used. It was found that, for dehydrated fully Ag⁺-exchanged faujasite-type zeolites, the silver atoms/ions were distributed among the six-ring sites (SI, SI', and SII for type X) and, for samples with high Al content, in the SIII locations. There is also the simultaneous occupancy of sites SI and SI' by linear (Ag⁺-Ag⁰-Ag⁺) clusters. In general, it appears that the Ag atoms/ions preferred the SI and SI' sites.

While it appears that the Ag⁺ ions prefer SI and SI' locations, it is also known that the Li⁺ ions also strongly prefer the SI' sites. A specific study to identify the location of Li⁺ and Ag⁺ cations mixed Li_xAg_y-zeolites has not yet been done. While not wishing to be held to any particular theory, it is thought that both of these sites are sterically inaccessible to the N₂ and O₂

molecules. Therefore, the formation of silver clusters in these locations may not have a strong effect on the overall adsorptive characteristics of the mixed $\text{Li}_x\text{Ag}_y\text{-X}$ zeolites. Therefore, it is expected that the clusters, in these mixed cation zeolites, are instead formed at the N_2 and O_2 accessible SII and/or SIII locations due to competition with the Li^+ cations for the preferred SI and SI' locations. Logically, Ag-cluster formation at the SII sites would most enhance the adsorptive characteristics of mixed $\text{Li}_x\text{Ag}_y\text{-X}$ zeolites since these sites have been shown to be non-interactive when occupied with Li^+ ions. The location of Ag in mixed $\text{Na}_x\text{Ag}_y\text{-A}$ zeolites was investigated and it was found that the Ag ions prefer six-ring sites (such as the SI, SI' and SII in the X zeolites). This may indicate a preference for the SII sites in type X zeolites when the SI and SI' sites may be unavailable (due to competition with Li^+). Another possibility is that the Ag clusters were formed at the SI-SI' sites, and due to the strong field gradient that is generated by Ag^+ , enhanced interactions with the N_2 molecules is still possible. This possibility would account for the fact that 1 Ag per unit cell resulted in the optimal sorbent because each Ag_3^{2+} cluster was shared by three supercage cavities.

25 The Nature of the Interaction

The total energy of physical adsorption ϕ_r , is the result of the interactions between the adsorbate molecules and interactions between the adsorbate molecules and the zeolite cavity wall. The ϕ_r is comprised of dispersive (D), repulsive (R), polarization (P), field-dipole (FD) interactions, field-quadrupole (FQ) interactions, and adsorbate-adsorbate energies and can be

written as per Equation (4). The adsorbates of interest in this evaluation (N_2 , O_2 and Ar) do not have permanent dipoles; and the coverages are low. Therefore, the field-dipole and adsorbate-adsorbate interactions can be ignored and Equation 4 can be reduced to Equation (5). Because the N_2 and O_2 molecules are very similar in size and have comparable polarizabilities, the dispersive, repulsive and polarization energies between the adsorbate and the extra-framework cations are very similar. The quadruple moment of the N_2 molecule is approximately four times that of the O_2 molecule and is primarily responsible for the difference in the adsorptive capacity for N_2 over that of O_2 . Argon, which does not have a quadruple moment, is more affected by the polarization energy; and for most zeolites, the Ar capacity is about the same as that of O_2 .

The very high heat of binding of the N_2 molecules at very low pressures is probably due to very high electrostatic fields near the exposed charged Ag-clusters and their interaction with the quadruple moment of the N_2 molecule. However, because there is also an increase in the adsorption of argon, which does not have a quadruple moment, these charged clusters must also contribute to the total energy of physical adsorption by increased van der Waals and field-induced dipole energies and could possibly have a higher polarizing power than that of isolated silver cations.

Physical adsorption, however, is likely not the only contribution to N_2 adsorption in silver-containing zeolites. Given the high isotheric heat of adsorption for N_2 on Ag₈₆-X-1.25 zeolites combined with a relatively slow desorption of N_2 on the same, some degree of weak π -

complexation is likely present. The π -complexation character of the interaction was confirmed by *ab initio* molecular orbital calculations using N_2 and Ag-X cluster model. This π -complexation character is also referred to as being weak chemisorption-assisted adsorption.

PSA Cycle Description

A standard five-step PSA cycle as is presently used in industry for air separation was used in this study. See U.S. Patent No. 5,074,892, Levitt, incorporated herein by reference in its entirety. The steps involved in each cycle are as follows: (step I) pressurization with the feed gas, namely 22% O_2 (mixture of O_2 and Ar) and 78% N_2 ; (step II) high pressure adsorption with the feed gas, or feed step; (step III) co-current depressurization; (step IV) countercurrent blowdown; and (step V) countercurrent low pressure purge with the product of the feed step (oxygen).

All the above steps were of equal duration (30 seconds); thus the time required for the completion of each PSA cycle was 2.5 minutes. The model assumed only two adsorbable components, O_2 and N_2 . The oxygen component (22%) was actually a mixture of O_2 and Ar which have very similar adsorption isotherms for the sorbents of interest. The product of each cycle was comprised of a volumetric mixture of the output stream of the feed step and the co-current depressurization step. A portion of this product stream was used to purge the bed countercurrently in step V.

In order to compare the performance of the LI_{96} -X-1.0 and the $LI_{95}Ag_1$ -X-1.0 sorbent developed in this

work, the product throughputs of the two sorbents were studied under two different cycle conditions using computer simulations. In order to facilitate a fair comparison of the sorbent performance, the cycle conditions were optimized such that the product purity and product recovery obtained were the same for both the sorbents in each respective simulation run. In this work, the product purity, product recovery and product throughput are defined as per Equations (6), (7), and (8).

The mathematical model and the numerical method used for the PSA simulations in this work will be explained to the extent necessary for fundamental understanding. The basic assumptions are as follows. The model used assumed the flow of a gaseous mixture of two components in a fixed bed packed with spherical adsorbent particles. The bed is considered to be adiabatic and diffusional resistance is assumed to be negligible since the diffusion of O_2 and N_2 in the adsorbents is essentially instantaneous, as observed in this study. Thus, there is local equilibrium between the gas and the solid phase of each gas component. Axial dispersion for mass and heat transfer is assumed but dispersion in the radial direction is taken to be negligible. Axial pressure drop is neglected and ideal gas law is assumed to hold since pressures involved are near atmospheric. Also the gas is assumed to have constant viscosity and heat capacity.

The pure component equilibrium amounts adsorbed on the respective adsorbents were fit using the well-known Langmuir isotherm with temperature dependent terms. The equilibrium loading under mixture conditions were

then predicted by the extended Langmuir equation in the simulation model as per Equation (9). The temperature dependence of the Langmuir parameters is assumed to be as per Equation (10). The values of the Langmuir equation terms for $\text{Li}_{96}\text{-X-1.0}$ ($\text{Li}_{94.5}\text{Na}_{1.5}\text{-X-1.0}$) and $\text{Li}_{95}\text{Ag}_1\text{-X-1.0}$ ($\text{Li}_{94.2}\text{Na}_{0.7}\text{Ag}_{1.1}\text{-X-1.0}$) sorbents, as well as the heats of adsorption are given in Table 1. Additional background of general interest, and not necessary to understanding of the invention may be found in Ind. Eng. Chem. Res. 36, 5358 (1997).

Simulation Results

The PSA bed characteristics and the operating conditions used are summarized in Table 2. The PSA cycle parameters were chosen as close to industrially acceptable values as possible. The pressure ratio, which is the ratio of the feed pressure (P_F) to the desorption pressure (P_L), is an important operating characteristic and it has been shown that a value of 3 suffices for an optimal PSA performance using the $\text{Li}_{96}\text{-X-1.0}$ sorbent. The same pressure ratio was employed for the comparison of the $\text{Li}_{96}\text{-X-1.0}$ ($\text{Li}_{94.5}\text{Na}_{1.5}\text{-X-1.0}$) and $\text{Li}_{95}\text{Ag}_1\text{-X-1.0}$ ($\text{Li}_{94.2}\text{Na}_{0.7}\text{Ag}_{1.1}\text{-X-1.0}$) sorbents in this work. Hereafter below, the nominal formulas $\text{Li}_{96}\text{-X-1.0}$ and $\text{Li}_{95}\text{Ag}_1\text{-X-1.0}$ are referred to. As can be seen from Table 3, run 1 had a feed pressure of 1.0 atm while run 2 was carried out at a higher feed pressure of 1.2 atm. The co-current depressurization pressure, feed velocity and purge velocity were optimized so as to obtain the same product purity and recovery for both the sorbents. As seen from the O_2 and N_2 isotherms in Figure 10, the $\text{Li}_{95}\text{Ag}_1\text{-X-1.0}$ sorbent has a higher capacity for N_2 . From the extended Langmuir isotherm (Equation 9), it follows that the

higher N₂ loading further suppresses the O₂ loading under mixture conditions, and as a result the working capacity of the Li_{9.5}Ag₁-X-1.0 sorbent further increases. Hence the amount of bed utilization (or the depth of propagation of the N₂ wavefront in the bed) of the Li_{9.5}Ag₁-X-1.0 sorbent was deeper than that of the Li_{9.6}-X-1.0 sorbent under identical cycle conditions. The higher capacity of the Li_{9.5}Ag₁-X-1.0 sorbent could be exploited by employing higher feed throughputs and lower co-current depressurization pressure without significantly lowering product purity and recovery. An important advantage of the higher capacity of the Li_{9.5}Ag₁-X-1.0 sorbent was a higher product throughput compared to that of the Li_{9.6}-X-1.0 sorbent when the other performance parameters (i.e., product purity and recovery) were kept the same. However, the heats of adsorption of the two components on the Li_{9.5}Ag₁-X-1.0 sorbent were also higher than those on the Li_{9.6}-X-1.0 sorbent. Severe temperature rise during adsorption adversely affects PSA separation performance. Hence a PSA simulation run became necessary to critically evaluate the importance of higher N₂ loading in case of Li_{9.5}Ag₁-X-1.0 sorbent and the accompanying heat effects.

The results of the simulation runs are shown in Table 3. It can be seen from run 1 (feed pressure: 1 atm), the O₂ product throughput obtained by using Li_{9.5}Ag₁-X-1.0 sorbent was 5.4×10^{-2} kg O₂/h/kg-sorbent compared to the throughput of 4.8×10^{-2} kgO₂/h/kg-sorbent offered by the Li_{9.6}-X-1.0 sorbent. The corresponding O₂ product purity and recovery were approximately 96% and 62% respectively. There is an improvement of 12.5% in the product throughput which translates into considerable savings in capital and operating costs since a higher product throughput implies a smaller bed requirement for

the same desired production. Another run was done at a different feed pressure of 1.2 atm with the cycle conditions optimized to produce O₂ product at 90.7% purity and 78% recovery. In this case as well, the product throughput of the Li₉₅Ag₁-X-1.0 sorbent was found to be higher (7×10^{-2} kg O₂/h/kg-sorbent), compared to that of the Li₉₆-X-1.0 sorbent (6.3×10^{-2} kg O₂/h/kg-sorbent). Thus, the product throughput of the Li₉₅Ag₁-X-1.0 sorbent is higher by 11% even at a lower O₂ product purity requirement. The values of the throughputs obtained in these experiments were found to have an order of magnitude agreement with those for Li₉₆-X-1.0 sorbent. From the simulated bed profiles, it was observed that temperature deviations from the feed temperature of 25°C due to the adsorption heat effects were about 17°C for the Li₉₅Ag₁-X-1.0 sorbent while it was only 12°C for the Li₉₆-X-1.0 sorbent. However, from the results it appears that the advantage of higher N₂ loading on the Li₉₅Ag₁-X-1.0 more than compensates the lowering of PSA performance due to higher heat effects. It is evident from the previous two examples that the Li₉₅Ag₁-X-1.0 sorbent is superior to the Li₉₆-X-1.0 sorbent for air separation by PSA.

Notation

	b	=	Langmuir parameter, atm ⁻¹
	D _{ax}	=	Axial dispersion coefficient in adsorbent particles, m ² /s
5	ΔH	=	Heat of adsorption, kcal/mol
	k ₁	=	Langmuir temperature dependence constant, mmol/g
	k ₂ , k ₄	=	Langmuir temperature dependence constant, K
10	k ₃	=	Langmuir temperature dependence constant, atm ⁻¹
	p	=	Partial pressure, atm
	P	=	Total pressure, atm
	q _m	=	Langmuir parameter, mmol/g/atm
15	q*	=	Equilibrium adsorbate loading, mmol/g
	T	=	Temperature, K
	U	=	Interstitial gas velocity, m/s

Subscripts

20	CD	=	Intermediate pressure corresponding to the co-current depressurization step
	H	=	Corresponding to the feed step
	i	=	Species 'i'
	j, k	=	Gas phase component index
	L	=	Low pressure corresponding to purge step

TABLE 1

Parameters in the Temperature Dependent Langmuir Isotherms
of N₂ and O₂ for the Li₉X-1.0 and Li₉Ag₁X-1.0 Adsorbents

Sorbent	Sorbate	k ₁ (mmol/g)	k ₂ (K)	k ₃ (atm ⁻¹)	k ₄ (K)	-ΔH (kcal/mol)
Li ₉ X-1.0	O ₂	1.14	239.2	2.20x10 ⁻³	1092	2.66
Li ₉ X-1.0	N ₂	1.69	134.4	1.19x10 ⁻³	1990	5.16
Li ₉ Ag ₁ X-1.0	O ₂	0.965	196.0	2.25x10 ⁻³	1212	3.00
Li ₉ Ag ₁ X-1.0	N ₂	2.12	64.82	7.78x10 ⁻³	1494	5.39

TABLE 2
Adsorption Bed Characteristics and Operating
Conditions Used in the PSA Simulations

5	Bed length	2.5 m
	Diameter of adsorber bed	1.0 m
	Bed external porosity	0.40
	Bed density	720 kg/m ³
	Heat capacity of gases	6.87 cal/mol/K
10	Heat capacity of bed	0.28 cal/g/K
	Wall temperature	298 K (ambient)
	Feed gas composition	78% N ₂ , 22% O ₂
	Feed gas temperature	298K
	Axial dispersion coefficient (D _{ax})	5x10 ⁻³ m ² /s

TABLE 3
PSA Simulation Operating Conditions and Results

Run 1. Sorbent	P _H (atm)	P _L (atm)	P _{CO} (atm)	U _H (m/s)	U _L (m/s)	O ₂ Product Purity (%)	O ₂ Product Recovery (%)	Product throughput (kg O ₂ /h/kg adsorbent)
LI ₉₆ -X-1.0	1.0	0.33	0.70	0.48	0.38	96.11	62.03	4.84x10 ⁻²
LI ₉₅ Ag ₁ -X-1.0	1.0	0.33	0.69	0.60	0.42	96.42	62.74	5.40x10 ⁻²
39								
Run 2. Sorbent	P _H (atm)	P _L (atm)	P _{CO} (atm)	U _H (m/s)	U _L (m/s)	O ₂ Product Purity (%)	O ₂ Product Recovery (%)	Product throughput (kg O ₂ /h/kg adsorbent)
LI ₉₆ -X-1.0	1.2	0.4	0.70	0.40	0.38	90.68	78.02	6.31x10 ⁻²
LI ₉₅ Ag ₁ -X-1.0	1.2	0.4	0.71	0.50	0.38	90.83	78.48	7.01x10 ⁻²

Table 4
Elemental Composition of Li₁Ag₇-X-1.0 Zeolite Samples*

Comp.	Sample 1		Sample 2		Sample 3	
	wt. %	+/-	wt. %	+/-	wt. %	+/-
Al	21.38	0.88	21.19	0.87	20.80	0.85
Ag	0.00	-	0.93	0.06	3.04	0.06
Na	0.28	0.02	0.14	0.01	0.10	0.01
Li	5.59	-	5.21	-	4.99	-

Comp.	Sample 4		Sample 5		Sample 6	
	wt. %	+/-	wt. %	+/-	wt. %	+/-
Al	19.45	0.81	18.37	0.75	11.91	0.49
Ag	9.57	0.16	15.64	0.12	55.49	0.27
Na	0.11	0.01	0.22	0.01	0.03	0.01
Li	4.76	-	3.85	-	0.00	-

*Lithium was measured by inductively coupled plasma-mass spectroscopy (ICP-MS); all others were measured by neutron activation analysis (NAA).

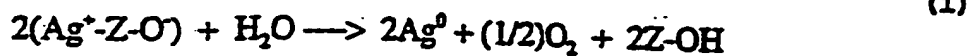
Table 5

Unit Cell Composition for Each of the Li₁Ag_x-X-1.0 Samples

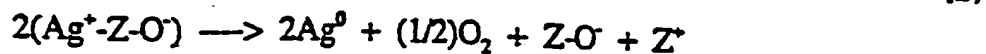
Comp.	1 atm/uc	2 atm/uc	3 atm/uc	4 atm/uc	5 atm/uc	6 atm/uc
Al	96.0	96.0	96.0	96.0	96.0	96.0
Ag	0.0	1.1	3.5	11.5	21.0	95.7
Na	1.5	0.7	0.5	0.6	1.2	0.3
Si	96.0	96.0	96.0	96.0	96.0	96.0
Li	94.5	94.2	92.0	83.9	73.8	0.0
O	384.0	384.0	384.0	384.0	384.0	384.0

EQUATIONS

(i) autoreduction in the presence of zeolite water (25 - 250°C)



(ii) autoreduction by oxygen from the zeolite lattice (127 - 380°C)



$$\Delta H_{ads} = R \left(\frac{d \ln P}{d(1/T)} \right)_n \quad (3)$$

$$\phi_T = -(\phi_D - \phi_R) - \phi_P - \phi_{FD} - \phi_{FQ} - \phi_{AA} \quad (4)$$

$$\phi_T = -(\phi_D - \phi_R) - \phi_P - \phi_{FQ} \quad (5)$$

$$\text{product purity} = \frac{(\text{amount of O}_2 \text{ from steps II and III})}{(\text{amount of N}_2 \text{ and O}_2 \text{ from steps II and III})} \quad (6)$$

$$\text{product recovery} = \frac{(\text{O}_2 \text{ from steps II and III}) - (\text{O}_2 \text{ used in step V})}{(\text{O}_2 \text{ fed in step I and step II})} \quad (7)$$

$$\text{product throughput} = \frac{(\text{amount of O}_2 \text{ produced per hour (kg/hr)})}{(\text{amount of adsorbent used in the bed (kg)})} \quad (8)$$

$$q_k^* = \frac{q_{mk} b_k p_k}{1 + \sum_{j=1}^m b_j p_j} \quad k=1,2 \quad (9)$$

$$q_m = k_1 \exp(k_2/T) \quad \text{and} \quad b = k_3 \exp(k_4/T) \quad (10)$$

The examples above demonstrate new methods for separating nitrogen from a mixture, and more specifically for accomplishing nitrogen separation from an air mixture using new and improved adsorbents. The zeolites of the invention, as demonstrated above, are lithium-based zeolites with silver cation or copper cation present at at least some of the exchangeable cationic sites. The presence of the exchanged cation at any of the sites demonstrated improved performance for adsorption over the non-exchanged zeolites. Without wishing to be held to any particular theory, it is believed that the lithium-based silver and copper exchanged zeolites of the invention achieve selective adsorption of nitrogen enhanced by weak chemical interaction through a type of pi-complexation bond. The effectiveness is clearly demonstrated in the above examples using the Ag^+ cation and the same results are obtainable with the Cu^+ cation. The Ag^+ ion and Cu^+ ion have the same electronic structure. That is, in the outer shell orbitals, the s-orbital (5s for Ag and 4s for Cu) is empty, whereas the d-orbitals (4d for Ag and 3d for Cu) are filled (with 10 electrons). This unique electronic structure is the reason that they can form the pi-complexation bonds with molecules that contain pi-electrons, such as olefins. For example, Ag^+ and Cu^+ have the same adsorption properties for olefins. Furthermore, Ag^+ in the AgX zeolite can also form pi-complexation with nitrogen (N_2) molecules because N_2 has a triple bond. Based on these two observations, it is evident that CuX zeolite forms pi-complexation with N_2 molecules.

As mentioned above, the X-zeolite unit cell can be represented by $(\text{AlO}_2)_{96}(\text{SiO}_2)_{96}$. There are 96 charges to each unit cell. The X zeolites, usable for the

invention, are not limited to this formula and may range from Si/Al ratio of about 1 to about 1.3. In one aspect the LSX zeolite having Si/Al ratio of about one, is preferred. In one aspect, the unit cell contains the preferred Li and Ag⁺ or Cu⁺ ions and has the formula
5 $\text{Li}_x\text{M}^{+1}_y(\text{AlO}_2)_{96}(\text{SiO}_2)_{96}$ where M⁺¹ is selected from Ag⁺ and Cu⁺ and mixtures thereof. In one preferred embodiment, the adsorbent is represented by this formula,
 $\text{Li}_x\text{M}^{+1}_y(\text{AlO}_2)_{96}(\text{SiO}_2)_{96}$, where y is in a range of about 0.5
10 to about 10 and x(Li) is 96-y. However, the invention is not limited to Si/Al = 1. As stated earlier, the ratio of Si/Al may range from about 1 to about 1.3, with good results using such Ag⁺ and Cu⁺ substituted lithium-based zeolites.

15 As stated earlier, some amount of other alkali metal (A⁺) and alkaline metal (Z⁺²) may also be included, as represented by the formula $\text{Li}_x\text{M}^{+1}_y\text{Z}^{+2}_a\text{A}^{+1}_b(\text{AlO}_2)_{96}(\text{SiO}_2)_{96}$. Here, the total positive charge for the cations Li, M, Z and A is 96;
20 $x+y+2a+b = 96$. The atomic portion of M is desirably less than 20, and preferably less than or equal to 10; and the portion of Li is desirably greater than 70 and preferably greater than 80. The atomic portion of cationic sites occupied by other metals (Z, A) is less than that
25 occupied by Li. In any case, the largest number of cationic sites is occupied by Li; then after Li, by Ag or Cu, and by Z and/or A, if any.

While this invention has been described in terms of certain embodiments thereof, it is not intended
30 that it be limited to the above description.

What Is Claimed Is:

1. A composition comprising lithium (Li) and metal(M)cation exchanged zeolite where said cation exchanged zeolite is selected from the group consisting of $\text{Li}_x\text{M}_y\text{X}$ zeolite, $\text{Li}_x\text{M}_y\text{LSX}$ zeolite and where said metal (M) is silver or copper and is in the form of dispersed clusters, x is greater than y , the sum of $x + y$ is less than or equal to the number of cation sites of said zeolite, and y is greater than zero.
2. The composition of claim 1 wherein M is silver presented in an atomic amount corresponding to up to about 20% of the cation sites.
3. The composition of claim 1 wherein M is silver presented in an atomic amount corresponding to up to about 10% of the cation sites.
4. The composition of claim 1 wherein the total number of said cation sites is 96, and Y is up to 20.
5. The composition of claim 1 wherein the total number of said cation sites is 96 and Y is up to 10.
6. The composition of claim 1 which is cation exchanged sodium zeolite where sodium is present in an atomic amount less than said silver.
7. The composition of claim 6 wherein the total number of cation sites is 96, lithium is present in an atomic amount greater than 70 and less than 96 atomic units, silver is present in an atomic amount greater than

0 and up to about 20 atomic units, and sodium is present in an atomic amount less than silver.

8. The composition of claim 1 wherein said clusters consist of partially metallic silver.

9. The composition of claim 8 wherein said clusters consist of n atoms of metal (M) collectively having a charge represented by the value $n-1$.

10. The composition of claim 9 wherein said clusters consist of 3 atoms of metal (M) collectively having a +2 charge, or 6 atoms of metal (M) collectively having a +5 charge.

11. The composition of claim 1 wherein said clusters consist of one selected from the group consisting of partially metallic copper and partially metallic silver.

12. The composition of claim 1 wherein M is copper present in atomic amount corresponding to up to about 20% of the cation sites.

13. The composition of claim 1 wherein M is copper present in an atomic amount corresponding to up to about 10% of the cation sites.

14. The composition of claim 1 which is cation exchanged sodium zeolite where sodium is present in an atomic amount less than said copper.

15. The composition of claim 14 wherein the total number of cation sites is 96, lithium is present in

an atomic amount greater than 70 and less than 96 atomic units, copper is present in an atomic amount greater than 0 and up to about 20 atomic units, and sodium is present in an atomic amount less than copper.

16. A process for selectively adsorbing nitrogen from a gas mixture thereof which comprises contacting said gas mixture with an adsorbent which comprises lithium (Li) and metal (M) cation exchanged zeolite where said zeolite is selected from the group consisting of $\text{Li}_x\text{M}_y\text{X}$ zeolite and $\text{Li}_x\text{M}_y\text{LSX}$ zeolite, and where said metal (M) is silver or copper and is in the form of dispersed clusters, x is greater than y , the sum of $x+y$ is less than or equal to the cation sites of said zeolite, and y is greater than 0.

17. The process of claim 16 wherein said zeolite is a lithium and silver exchanged sodium zeolite, said method further comprising contacting said gaseous mixture with said zeolite at a selected temperature and pressure, thereby producing a non-adsorbed component and a nitrogen-rich adsorbed component; and changing at least one of said pressure and temperature to thereby release said nitrogen-rich component from said adsorbent.

18. A process for preparing a composition comprising lithium and metal (M) cation exchanged zeolite where M is in the form of dispersed clusters associated with a plurality of said cation exchanged sites, said method comprising the steps of:

- a. providing a sodium zeolite selected from the group consisting of Na-X zeolite and Na-LSX zeolite;
- b. exchanging a plurality of Na^{1+} ions with Li^{1+} ions;

c. exchanging a portion of said Li^{1+} ions with M^{1+} ions;

d. heat treating the M^{1+} exchanged zeolite of step (c) at a temperature of greater than about 400 degrees centigrade in a non-oxidizing atmosphere to reduce a portion of said M^{1+} ions to M^0 , thereby forming said dispersed clusters.

19. The process of claim 18 wherein in step (c) M^{1+} is Ag^{1+} , and step (d) is conducted at a temperature in a range of about 450° to about 500°C.

20. The process of claim 18 wherein M^{1+} is Cu^{+1} and step (c) is conducted by first exchanging Li^{1+} ions with Cu^{2+} ions and then reducing said Cu^{2+} ions to Cu^{1+} ions.

21. The process of claim 18 wherein in step (d) the non-oxidizing atmosphere is an inert atmosphere, reducing atmosphere, or a vacuum.

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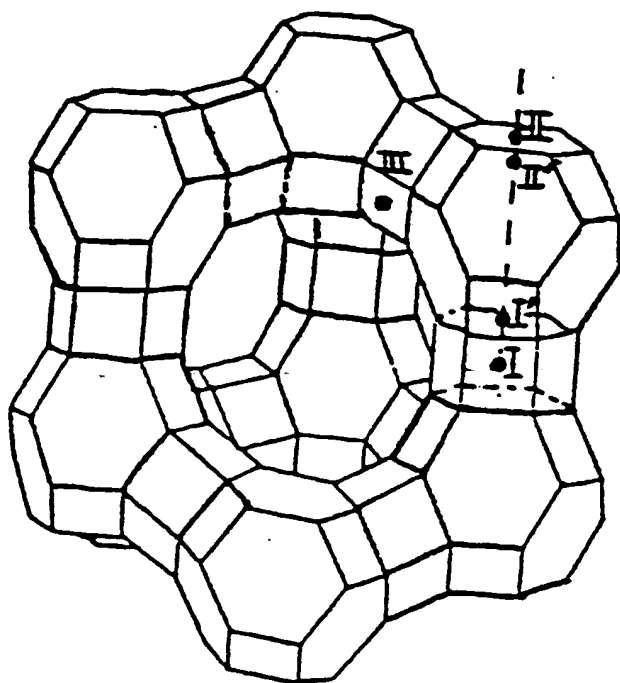


Figure 1. Unit cell of faujasite-type (X and Y) zeolites including cation sites.

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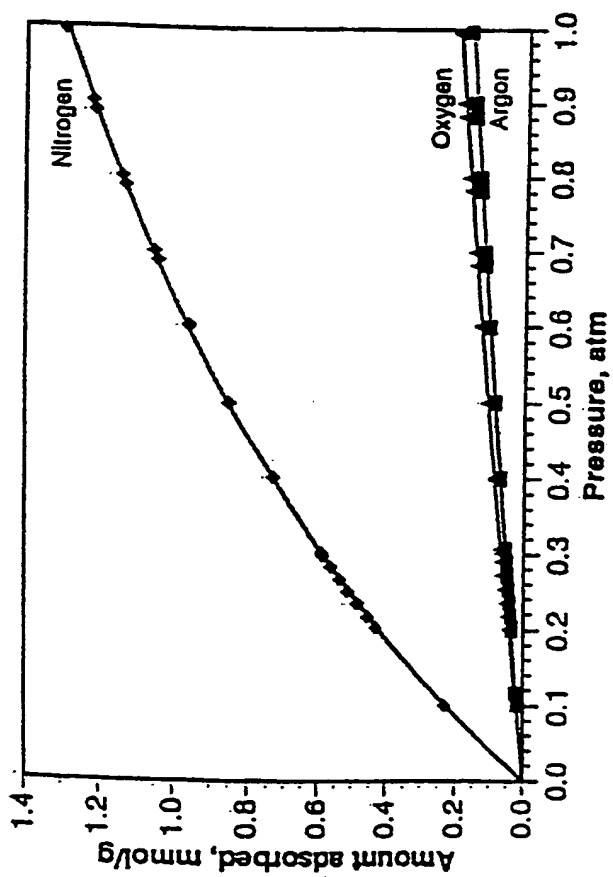


Figure 2. Adsorption isotherms for N_2 , O_2 and Ar measured at 25°C for $Li_{0.5}Na_{1.5}X-1.0$ dehydrated *in vacuo* at 350°C.

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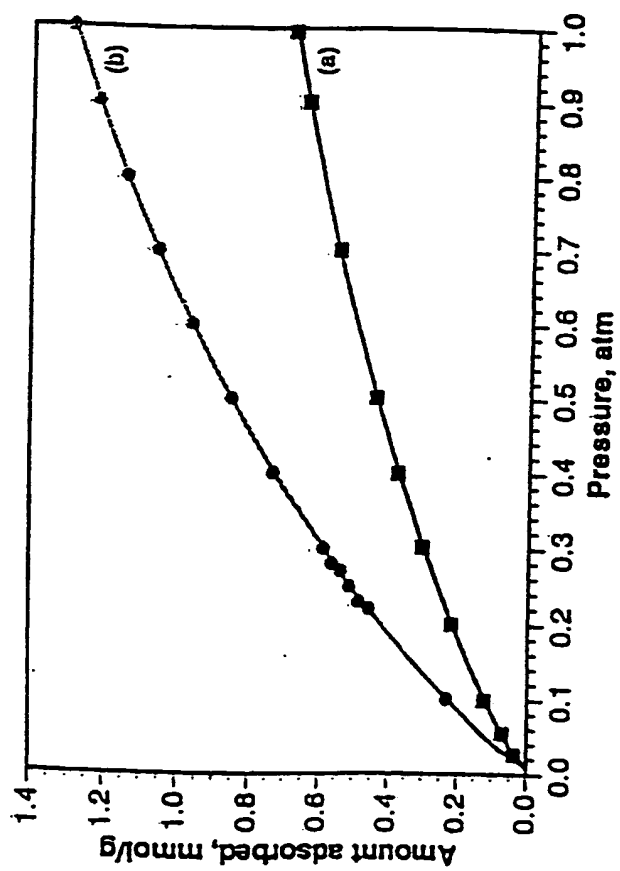


Figure 3. N₂ adsorption isotherms, measured at 25°C for (a) Li_{0.94}Na_{1.5}X-1.0 and (b) Li_{0.77}Na_{0.75}X-1.25. Both materials were dehydrated *in vacuo* at 350°C.

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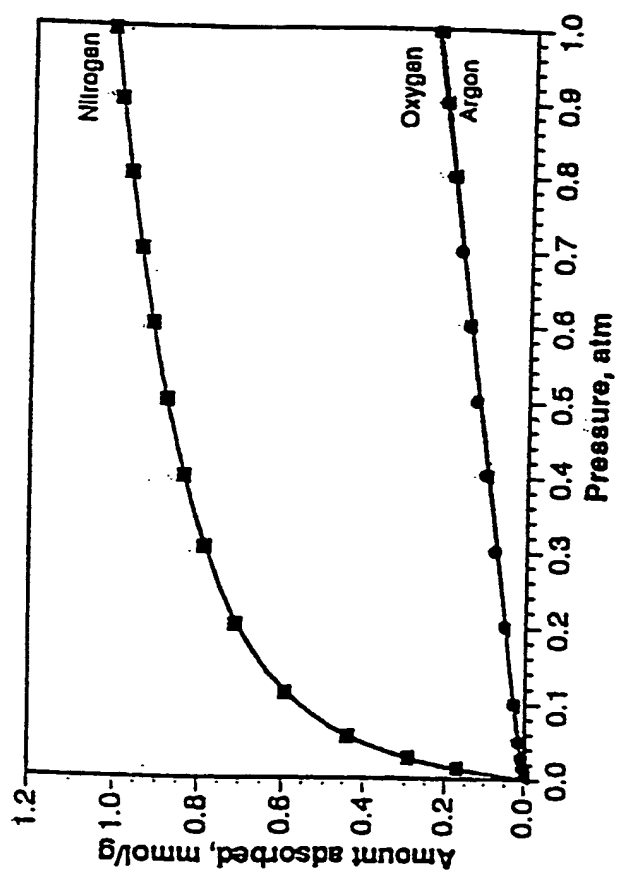


Figure 4. Adsorption isotherms measured at 25°C for N₂, O₂ and Ar on Ag_{85.7}Na_{0.3}-X-1.0 dehydrated *in vacuo* at 450°C.

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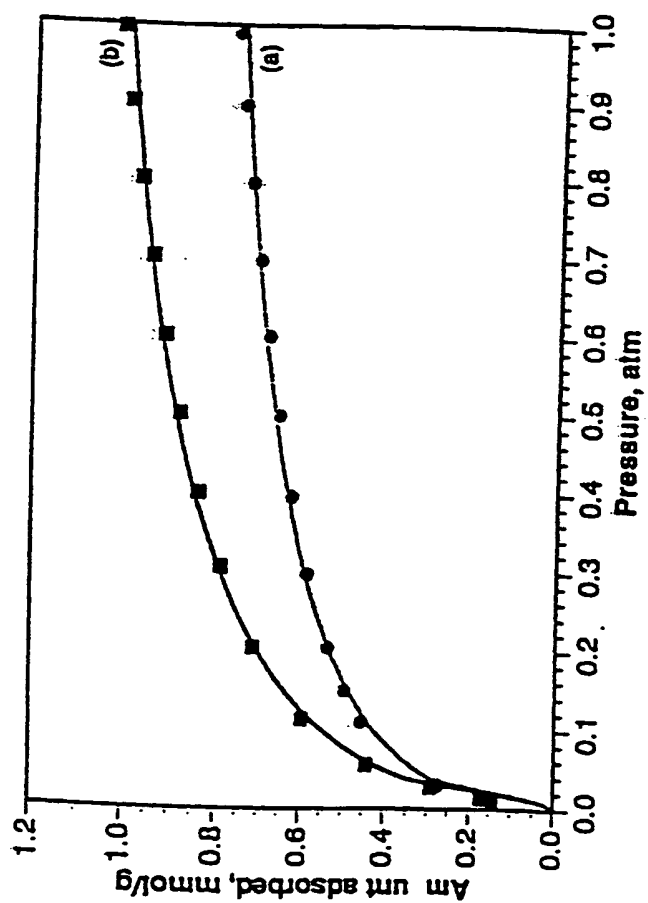


Figure 5. N₂ adsorption isotherms, measured at 25°C, for (a) Ag₆₅,Na_{0.3}-X-1.25 and (b) Li₉₅,Na_{0.3}-X-1.0. Both materials were dehydrated *in vacuo* at 450°C.

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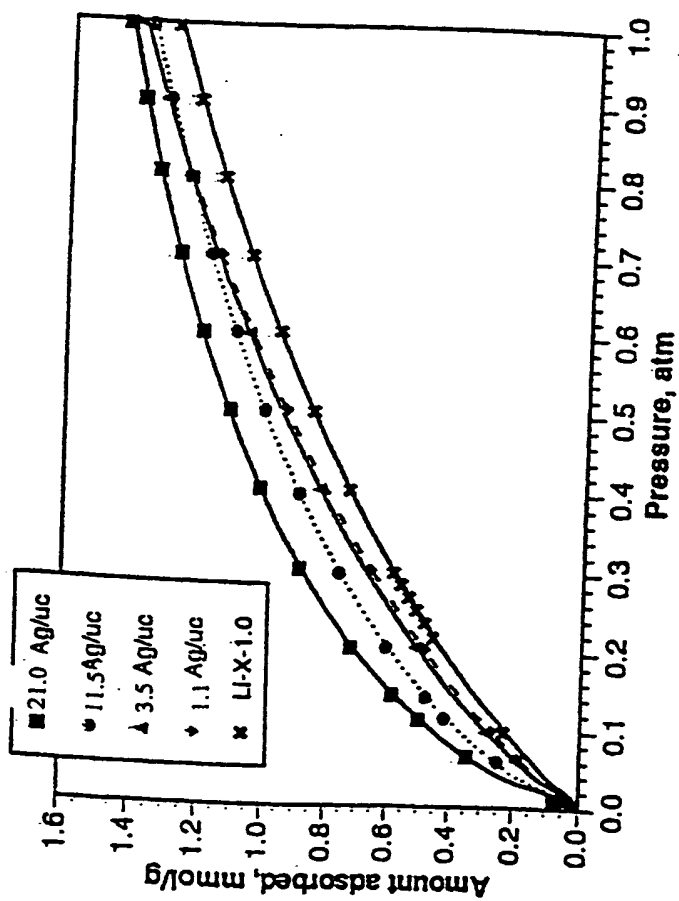


Figure 6. N₂ adsorption isotherm, measured at 25°C, for (LiAg-X-1.0 zeolites dehydrated *in vacuo* at 450°C. This shows the addition of increasing amounts of Ag results in a change in the general aspect of isotherm toward that of the fully Ag⁺-exchanged material.

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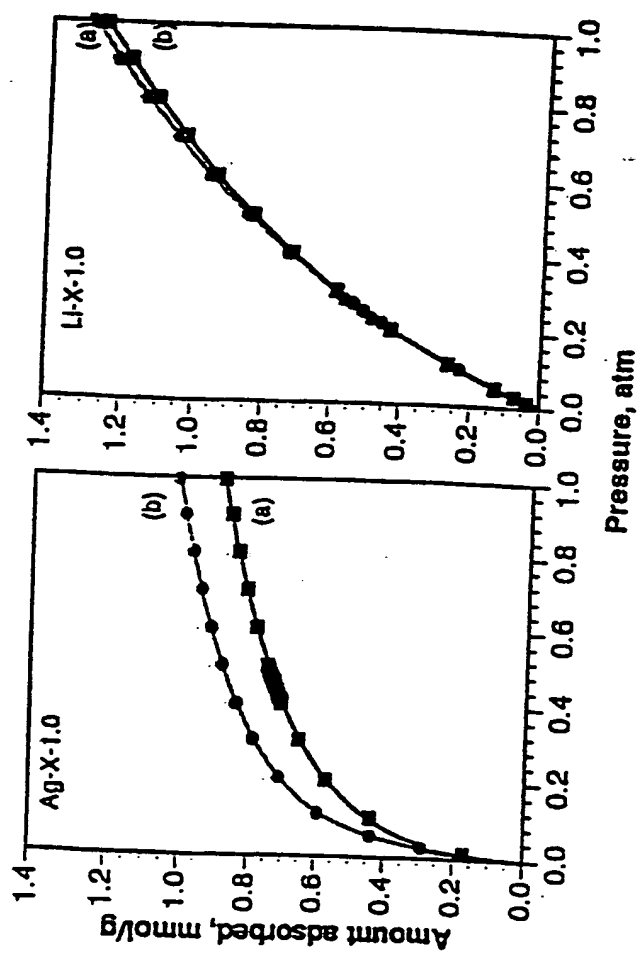


Figure 7. N₂ adsorption isotherm, measured at 25°C, for Ag_{99.7}Na_{0.3}X-1.0 (left, Ag-X-1.0) and Li_{99.7}Na_{0.3}X-1.0 (right, Li-X-1.0). The materials were dehydrated *in vacuo* at (a) 350°C and (b) 450°C.

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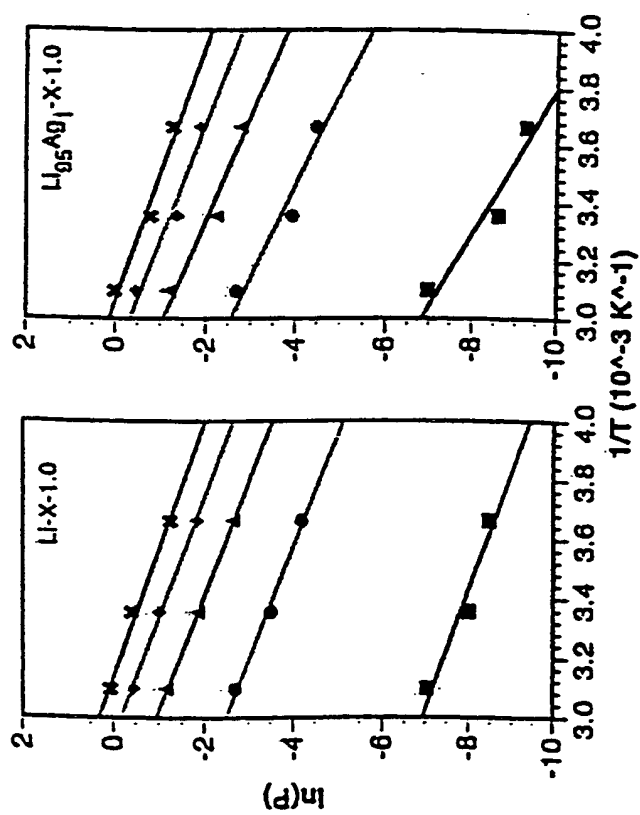


Figure 8. $\ln(P)$ vs $1/T$ at different coverages for $\text{Li}_{94.5}\text{Na}_{1.5}\text{-X-1.0}$ (left, Li-X-1) and $\text{Li}_{94.2}\text{Na}_{0.7}\text{Ag}_{1.1}\text{-X-1.0}$ (right, $\text{Li}_{95}\text{Ag}_1\text{-X-1}$).

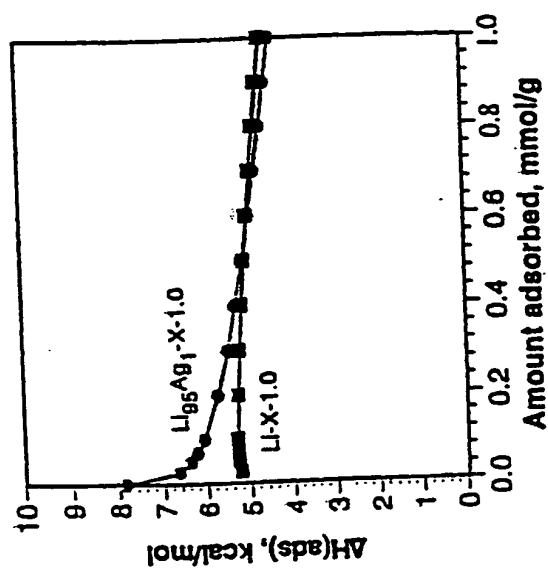


Figure 9. Isosteric heats of adsorption of N_2 for $\text{Li}_{94.3}\text{Na}_{1.5}\text{X-1.0}$ (Li-X) and $\text{Li}_{94.2}\text{Na}_{0.7}\text{Ag}_{1.1}\text{-X-1.0}$ ($\text{Li}_{95}\text{Ag}_1\text{-X}$).

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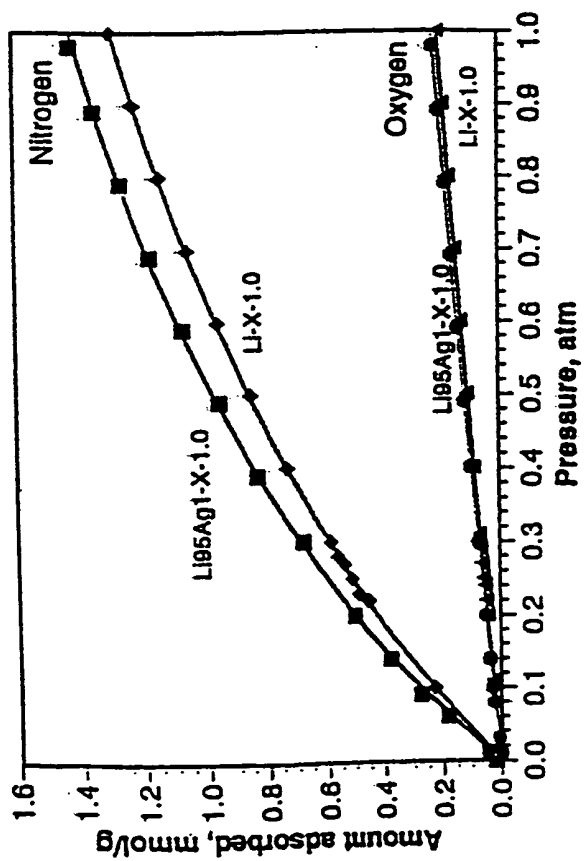


Figure 10. N₂ and O₂ isotherms for Li_{0.94}Na_{0.7}Ag_{1.1}-X-1.0 (Li_{0.93}Ag_{1-X}) dehydrated *in vacuo* at 450°C and for Li_{0.93}Na_{1.5}X-1.0 (Li-X) dehydrated *in vacuo* at 350°C. All isotherms were measured at 25°C.